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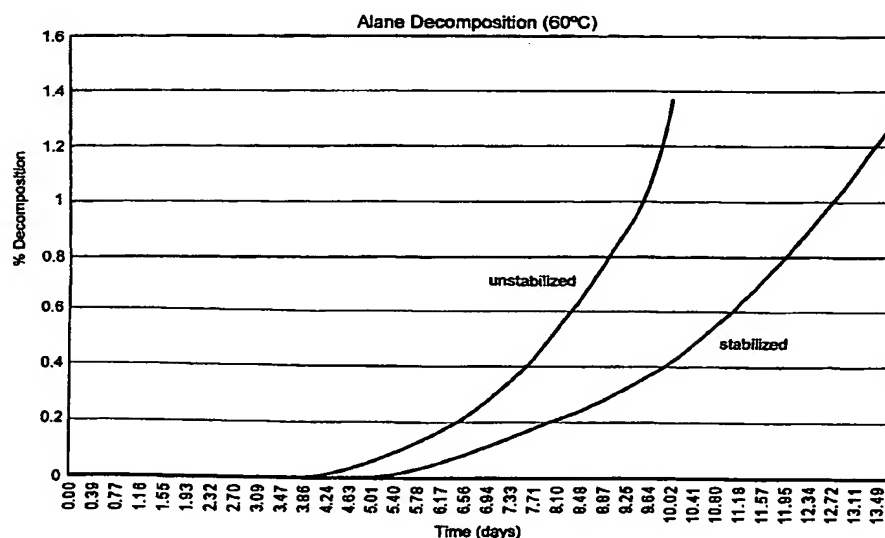
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- (71) Applicant: SRI INTERNATIONAL [US/US]; 333 Ravenswood Avenue, Menlo Park, CA 94025 (US). For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
- (72) Inventors: PETRIE, Mark, A.; 10368 Leola Court #1, Cupertino, CA 95014 (US). BOTTARO, Jeffrey, C.; 532 Tyrella #39, Mountain View, CA 94043 (US). PENWELL, Paul, E.; 719 Floralis, Palo Alto, CA 94306 (US).

(54) Title: PREPARATION OF ALUMINUM HYDRIDE POLYMORPHS, PARTICULARLY STABILIZED ALPHA-ALH₃



(57) Abstract: The present invention features methods for preparing stabilized α -AlH₃ and α -AlH₃, compositions containing these alane polymorphs, e.g., energetic compositions such as rocket propellants, and methods for using the novel polymorphs as chemical reducing agents, polymerization catalysts, and as a hydrogen source in fuel cells and batteries. The method produces stabilized alane by treating α -AlH₃ with an acidic solution that optionally contains a stabilizing agent such as an electron donor, an electron acceptor, or a compound which coordinates the Al³⁺ ion.

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PREPARATION OF ALUMINUM HYDRIDE POLYMORPHS,
PARTICULARLY STABILIZED ALPHA- AlH_3

REFERENCE TO GOVERNMENT SUPPORT

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TECHNICAL FIELD

The present invention relates generally to aluminum hydride, or "alane," and more particularly relates to a novel method for preparing aluminum hydride polymorphs such as $\alpha\text{-AlH}_3$ and $\alpha'\text{-AlH}_3$. The invention additionally relates to a stabilized form of $\alpha\text{-AlH}_3$, to energetic compositions, particularly propellant compositions, containing, as a
15 fuel, stabilized $\alpha\text{-AlH}_3$ and/or $\alpha'\text{-AlH}_3$ prepared using the method of the invention, and to methods of using the alane polymorphs prepared herein as chemical reducing agents, as polymerization catalysts, and as a source of hydrogen gas such as in batteries and fuel cells.

20

BACKGROUND ART

Aluminum hydride, also referred to as "alane," is usually prepared as a solution by the reaction of lithium aluminum hydride with aluminum trichloride. A.E. Finholt et al. (1947) *J. Am. Chem. Soc.* 69:1199. The alane-containing solution, however, is not stable,
25 as an alane•ether complex precipitates from solution shortly after preparation. In addition, attempts to isolate the nonsolvated form of alane from the ether solution result in the decomposition of the complex to aluminum and hydrogen. M.J. Rice Jr. et al. (1956) Contract ONR-494(04) ASTIA No. 106967, U.S. Office of Naval Research.

In a method for preparing non-solvated alane, alane•etherate may be desolvated in the presence of a small amount of lithium aluminum hydride. See, for example, A.N. Tskhai et al. (1992) *Rus. J. Inorg. Chem.* 37:877, and U.S. Patent No. 3,801,657 to Scruggs. Non-solvated alane exhibits six crystalline phases, with each having different physical properties. The phase designated as α' -alane is essentially non-solvated and appears under a polarizing microscope as small multiple needles growing from single points to form fuzzy balls. The γ phase appears as bundles of fused needles. The γ phase is produced in conjunction with the β phase, and both γ - and β -alane are metastable nonsolvated phases that convert to the more stable α -alane upon heating. The α -alane is the most stable, and is characterized by hexagonal or cubic shaped crystals that are typically 50 - 100 μm in size. The other two forms, designated δ - and ϵ -alane, are apparently formed when a trace of water is present during crystallization, and the ζ -alane is prepared by crystallizing from di-n-propyl ether. The α' , δ , ϵ and ζ polymorphs do not convert to the α -alane and are less thermally stable than the α -form. For a discussion of the various polymorphs, reference may be had to F. M. Brower et al. (1976) *J. Am. Chem. Soc.* 98:2450.

Alane consists of about 10% hydrogen by weight, thereby providing a higher density of hydrogen than liquid hydrogen. Because of the high hydrogen density and the highly exothermic combustion of aluminum and hydrogen, alane can be used as a fuel for solid propellants or as an explosive.

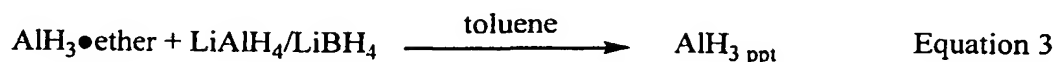
Solvated alane can be synthesized by the reaction of LiAlH_4 with aluminum chloride, resulting in the alane•etherate complex (equation 1).



In an alternative synthesis, LiAlH_4 is reacted with sulfuric acid to give the alane•etherate complex (equation 2).



The AlH_3 -ether complex is then treated with a mixture of LiAlH_4 and LiBH_4 , and heated (equation 3).



The combination of $\text{LiBH}_4/\text{LiAlH}_4$ enables use of a lower processing temperature, and α -
5 alane is the final product after heating at 65 °C under vacuum. In an alternative synthesis, Bulychev reports that α -alane can be prepared at pressures greater than 2.6 GPa and at temperatures in the range of 220- 250 °C. B.M. Bulychev et al. (1998) *Russ. J. Inorg. Chem.* 43:829. Under those conditions, apparently only the α -alane form is observed.

In addition, alane can be directly synthesized by metathesis of aluminum alkyls
10 followed by removal of the alkylaluminum byproduct in vacuum (equation 4).



Still another method of preparing nonsolvated alane is by bombarding an ultrapure aluminum target with hydrogen ions. However, alane thus produced has poor crystallinity.

One of the obstacles to large scale production of α -alane is the handling of the
15 diethyl ether solution of the alane•ether complex. At concentrations of about 0.5 M or higher and temperatures above 0 °C, the alane•ether phase prematurely precipitates out of solution. In addition, α -alane can be contaminated with other phases of alane, and is not stable over time as the complex decomposes to hydrogen and aluminum.

Thus, although alane is potentially promising as a high energy density fuel,
20 because of its high hydrogen density and the highly exothermic combustion of aluminum and hydrogen, the lack of a suitable method for synthesizing alane in a stabilized form has severely limited its applicability.

BRIEF DESCRIPTION OF THE INVENTION

Accordingly, it is a primary object of the invention to address the above-mentioned need in the art and provide a method for synthesizing α -alane in a stabilized form.

5 It is another object of the invention to provide stabilized α -alane as a novel composition of matter, prepared using the aforementioned method.

It is an additional object of the invention to provide a method for synthesizing α' -alane.

10 It is a further object of the invention to provide energetic compositions containing stabilized α -alane or α' -alane, prepared using the methods described herein.

It is still a further object of the invention to provide such energetic compositions in the form of a propellant composition.

15 It is also an object of the invention to provide methods for using stabilized α -alane or α' -alane, prepared using the methods described herein, as an energy dense fuel, as a chemical reducing agent, as a polymerization catalyst, and as a source of hydrogen gas such as in batteries and fuel cells.

20 Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention.

In one embodiment, then, the invention relates to a method for preparing stabilized α - AlH_3 , wherein: (a) an alkali metal hydride is initially reacted with AlCl_3 in diethyl ether to form an initial AlH_3 product and an alkali metal chloride; (b) the reaction mixture is filtered to remove the alkali metal chloride; (c) an excess of toluene is added to the filtrate of step (b), resulting in a diethyl ether-toluene solution; (d) the diethyl ether-toluene solution is heated and distilled to reduce the amount of diethyl ether in solution, until a precipitate is formed; (e) the precipitate is isolated; and (f) the isolated precipitate is added to an acidic solution effective to dissolve and thus remove materials other than α - AlH_3 . In a preferred embodiment, the acidic solution contains an α - AlH_3 stabilizing agent, e.g., a compound that coordinates to the Al^{3+} ion, an electron donor, or an electron acceptor.

25

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In another embodiment, the invention provides a method for synthesizing α' - AlH_3 , wherein (a) an alkali metal hydride is initially reacted with AlCl_3 in diethyl ether to form an initial AlH_3 product and an alkali metal chloride; (b) the reaction mixture is filtered to remove the alkali metal chloride; (c) an additional alkali metal hydride and an excess of toluene are added to the filtrate of step (b), providing a diethyl ether solution containing α' - AlH_3 and optionally other AlH_3 polymorphs; and (d) removing the α' - AlH_3 is from the solution.

In a further embodiment of the invention, a propellant composition is provided containing fuel, a binder material, and an oxidizer, wherein the fuel is a stabilized α - AlH_3 product or an α' - AlH_3 product prepared using the aforementioned techniques. The alane polymorphs of the invention are compatible with a wide range of binder materials, oxidizers, secondary fuels, and other propellant components, and provide for a propellant that is chemically and physically stable over an extended period of time.

The invention also provides methods for using the stabilized α - AlH_3 product and the α' - AlH_3 product in other contexts. For example, an alane polymorph as synthesized herein may be used as a chemical reducing agent, in any context wherein a hydride donor is appropriate to bring about reduction, e.g., in reducing unsaturated carbon-carbon bonds such as present in alkenes and alkynes, in reducing carbonyl-containing moieties such as ketones, aldehydes, carboxylic acids, and acid chlorides, in converting halides to hydrido moieties, and the like. The present alane polymorphs may also be used as polymerization catalysts, typically in catalyzing addition polymerization reactions, e.g., the polymerization of olefins, and as a hydrogen source in fuel cells and batteries.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph illustrating the relative stability of α -alane prepared using a prior art method and α -alane prepared using the method of the invention.

MODES FOR CARRYING OUT THE INVENTION

DEFINITIONS AND NOMENCLATURE:

Before the present methods, compounds and compositions are disclosed and
5 described, it is to be understood that unless otherwise indicated this invention is not
limited to the use of specific reagents, reaction conditions, composition components, or the
like, as such may vary. It is also to be understood that the terminology used herein is for
the purpose of describing particular embodiments only and is not intended to be limiting.

It must be noted that, as used in the specification and the appended claims, the
10 singular forms "a," "an" and "the" include plural referents unless the context clearly
dictates otherwise. Thus, for example, reference to "a stabilizing agent" includes mixtures
of stabilizing agents, reference to "alane" can refer to more than one polymorph of AlH_3 ,
and the like.

The term "alane" refers to aluminum hydride, having the formula AlH_3 , and
15 includes all the polymorphs such as $\alpha\text{-AlH}_3$, $\alpha'\text{-AlH}_3$, $\delta\text{-AlH}_3$, and the like.

The term "stabilizing agent" refers to compound that tends to inhibit the
decomposition of α -alane. The stabilizing agent can be an electron acceptor, an electron
donor, or a compound which coordinates to the Al^{3+} ion.

The term "stabilized" when used to refer to the α -alane product of the invention
20 indicates that the product is substantially more stable than α -alane products of the prior art
(i.e., α -alane prepared without the use of an acid wash workup and/or without stabilizing
agents as disclosed herein). That is, "unstabilized" α -alane rapidly decomposes to
hydrogen and aluminum, while the stabilized α -alane of the invention does not. "Stability"
refers to both thermal stability and stability at ambient temperature. With respect to
25 thermal stability, as illustrated in Figure 1, the "stabilized" α -alane of the invention is less
than 1% decomposed after twelve days at 60°C , while decomposition of the unstabilized
product at that point is virtually complete (as may be inferred from the graph).

METHOD FOR PREPARING STABILIZED $\alpha\text{-AlH}_3$:

30 In a first embodiment of the invention, a method is provided for preparing
stabilized $\alpha\text{-AlH}_3$. An alane•ether complex, $\text{AlH}_3\cdot\text{Et}_2\text{O}$, is initially prepared. Aluminum

chloride is dissolved in diethyl ether, and an alkali metal hydride is then added. The alkali metal hydride can be, for example, lithium hydride (LiH), sodium hydride (NaH), potassium hydride (KH), calcium hydride (CaH_2), magnesium hydride (MgH_2), sodium borohydride (NaBH_4), lithium borohydride (LiBH_4), lithium aluminum hydride (LiAlH_4), sodium aluminum hydride (NaAlH_4), or combinations thereof. In general, LiAlH_4 , LiBH_4 , and combinations thereof are the preferred metal hydrides. The relative proportion of the alkali metal hydride to aluminum chloride is not critical; however, to assure substantially complete conversion of AlCl_3 to AlH_3 , an excess of the alkali metal hydride is preferably used, such as a molar ratio of about 3:1 to 4.5:1, preferably 3.2:1 to 4:1 (LiAlH_4 : AlH_3).

The reaction is preferably carried out at a temperature of less than about 0°C , and a temperature of about -10°C has been found to be optimal. The solution, upon substantial completion of reaction, is filtered to remove the alkali metal chloride, a by-product of the reaction. At this point, it is desirable although not essential to introduce an additional alkali metal hydride into the reaction mixture, e.g., NaAlH_4 or NaBH_4 , to further assist in crystallization of the product, thereby enabling removal of impurities, particularly the slightly soluble alkali metal chloride that results along with the AlH_3 etherate complex. The additional alkali metal hydride may or may not be the same as the alkali metal hydride used initially. In this case, a further filtration step is conducted. Then, a large excess of an aromatic organic solvent, e.g., benzene, toluene, xylene, anisole, or the like, is added to the filtrate, assisting in the removal of impurities from the reaction mixture; benzene and toluene are preferred solvents. Alternatively, the reaction can be carried out in a solvent mixture of the ether and the aromatic solvent.

Crystals of $\alpha\text{-AlH}_3$ can then be obtained by first distilling the ether-aromatic solvent solution to reduce the amount of ether to less than about 10% by volume, preferably by heating, under vacuum, and then heating the solution until a precipitate is formed. Optimally, two cycles of heating are applied to the solution, the first at a temperature in the range of about $82\text{-}85^\circ\text{C}$, for about 1-2 hours, and the second at a temperature in the range of about $90\text{-}93^\circ\text{C}$, for about 20-40 minutes. Crystals of $\alpha\text{-AlH}_3$ prepared by this method typically reach a size of between 50 - 100 μm .

The α -alane precipitate is stabilized using an acid wash workup. α -Alane is slowly added to a well-stirred dilute acid solution. The acid is chosen from hydrochloric

acid, hydrogen fluoride acid, hydrogen bromide acid, phosphoric acid, perchloric acid, sulfuric acid, boric acid, and the like, but most preferably is hydrochloric acid. The concentration of the acid is about 1-25% v/v, preferably about 5-15% v/v, most preferably about 10% v/v. The α -alane-containing dilute acid solution is filtered and rinsed, e.g., with
5 water, an organic alcohol, and an organic solvent. The organic alcohol may be, for example, methanol, ethanol, n-propanol, isopropanol, n-butanol, s-butanol, or t-butanol, and the organic solvent is an ether, preferably diethyl ether. The acid wash workup removes residual impurities such as LiCl, NaBH₄, LiBH₄, LiAlH₄, and the like, as well as any remaining reactive alane polymorphs. In addition, the acid wash provides an Al(OH)₃
10 and Al₂O₃ coating on the α -alane material, thereby stabilizing the product.

In addition, the surface of the α -alane precipitate can be coated with a surface stabilizing agent. The stabilizing agent may be, for example, a compound that coordinates the Al³⁺ ion. In theory, the Al³⁺ ions catalyze the surface decomposition of the α -alane, leading to degradation of the bulk sample. Thus, compounds that coordinate Al³⁺ ions
15 prevent the decomposition of α -alane, thereby leading to a more stable product. Suitable stabilizing agents that coordinate the Al³⁺ ion are typically polyhydric monomers and polymers and include, but are not limited to, aluminon™ (aurintricarboxylic acid triammonium salt), 8-hydroxyquinoline, and catechol. The amount of the surface stabilizer provided on the aluminum hydride is about 0.1 to 10% of the total weight,
20 preferably about 1 to 5% of the total weight. The surface stabilizers can be applied to the surface of alane during the synthesis of alane, during the acid workup process, or after the α -alane has been isolated. Thus, for example, a surface stabilizer can be added during the heating cycles, during the acid wash step, or by slow evaporation of a slurry of alane, e.g., a methanol slurry of alane, containing 1 to 5% of the stabilizers.

25 Additionally, α -alane can be doped with other stabilizers that are electron donors or electron acceptors. In theory, photochemical or thermal decomposition of alane is caused by the initial formation of positive ion/electron holes that result in hydrogen evolution. Mobile electrons are theorized to catalyze the decomposition of alane to aluminum and hydrogen via this mechanism. Thus, the addition of electron acceptors and
30 donors, optionally with a complexing agent that is a Lewis acid or a Lewis base, inhibits the decomposition of α -alane. The electron donor or acceptor stabilizers include

tetrachlorobenzoquinone, diphenylamine, tetracyano-ethylene, 7,7,8,8-tetracyanoquinodimethane, tetrathiofulvalene, tetrakis(dimethylamino)-ethylene, and the like. The total amount of the electron donor or acceptor stabilizers provided on the α -alane is about 0.1 to 10% of the total weight, preferably about 1-5% of the total weight. The
5 alane is preferably doped with the stabilizers during the crystallization of the α -alane phase, although, as described above, the stabilizers can be applied to the surface of alane during the synthesis of alane, during the acid workup process, or after the α -alane has been isolated. In addition, band gap attenuators, that include Ti-, Si-, and P-containing derivatives, can be added during synthesis or to the surface. The band gap attenuators
10 inhibit radical reactions.

METHOD FOR PREPARING α' - AlH_3 :

Crystals of α' - AlH_3 can be prepared by reacting an alkali metal hydride with AlCl_3 in a solution of diethyl ether and removing the alkali metal chloride from the reaction mixture
15 by filtration, as described in the preceding section. The process initially yields solvated alane. The solvated alane, in an ethereal solution containing an excess of an alkali metal hydride or borohydride, preferably NaBH_4 , NaAlH_4 , or LiBH_4 , most preferably LiBH_4 , is heated to about 80 °C under pressure to give primarily the nonsolvated alane phase designated α' - AlH_3 . Other AlH_3 polymorphs may be present in the solution. In addition, mixtures of the nonsolvated α -
20 and γ - AlH_3 can be prepared by slowly distilling off the ether during the heating process such that the concentration of alane approaches the saturation level.

ENERGETIC COMPOSITIONS:

A primary use of stabilized α -alane and α' -alane as prepared herein is in the
25 manufacture of explosive and propellant compositions, particularly in the manufacture of rocket propellant compositions, including solid and solution propellants, typically solid propellants. Alane is known to be useful as an energy dense fuel in propellant formulations; however, problems with stability have arisen, as noted previously herein. The use of alane prepared using the method of the invention significantly increases the stability of the
30 propellant composition, and thus provides an important advance in the field.

The propellant compositions herein, in addition to alane, contain a binder material

and an oxidizer. Examples of binder materials for use in propellant applications include but are not limited to polyoxetanes, polyglycidyl azide, hydroxyl-terminated polybutadiene, polybutadiene-acrylonitrileacrylic acid terpolymer, polyethers, polyglycidyl nitrate, and polycaprolactone; see, e.g., U.S. Patent No. 5,292,387 to Highsmith et al. Examples of
5 oxidizers that may be incorporated into the compositions include, but are not limited to, ammonium nitrate (AN), phase-stabilized ammonium nitrate (PSAN), ammonium dinitramide (AND), potassium nitrate (KN), potassium dinitramide (KDN), sodium peroxide (Na_2O_2), ammonium perchlorate (AP), KDN-AN, a cocrystallized form of potassium dinitramide and ammonium nitrate, cyclo-1,3,5-tri-methylene-2,4,6-trinitramine (RDX or cyclonite), high
10 melting explosives (HMX), diaminodinitro ethylene (DADNE), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20, also known as HNIW), and combinations thereof. The propellant may also contain an additional fuel material, typically a metallic fuel comprised of, for example, aluminum, beryllium, boron, magnesium, zirconium, or mixtures or alloys thereof. Other components for incorporation into propellant compositions include plasticizers,
15 burn rate modifiers, ballistic additives, and the like. In general, propellant compositions of the invention are prepared by blending the stabilized alane with the oxidizer, the binder, and a curing agent effective to cure the admixture, e.g., hexane 1,6-diisocyanate, toluene diisocyanate, isophorone diisocyanate, or the like. Proportions of fuel and oxidizer can be varied to optimize performance, as will be appreciated by those skilled in the art.

20

OTHER USES:

The present compounds may also be used as reducing agents, as polymerization catalysts, and as a hydrogen source in fuel cells and batteries.

Use as reducing agent: An alane polymorph as synthesized herein may be used as a
25 chemical reducing agent in any context wherein a hydride donor is appropriate to bring about reduction, e.g., in reducing unsaturated carbon-carbon bonds such as present in alkenes and alkynes, in reducing carbonyl-containing moieties such as ketones, aldehydes, carboxylic acids, esters, amides acid chlorides, in converting halides to hydrido moieties, and the like. Typically, a compound to be reduced is dissolved in an organic solvent and reacted with the
30 stabilized α -alane of the invention, or with α' -alane as prepared herein, and the reaction product then isolated and purified.

Use in Polymerization: The alane polymorphs prepared using the methods described herein may also be used as polymerization catalysts, typically in catalyzing addition polymerization reactions, e.g., the polymerization of olefins. Generally, polymerization using the novel alane polymorphs as catalysts involves conventional processes wherein selected monomers are contacted with the alane polymorph under reaction conditions effective to provide the desired polymer composition. Polymerization may be carried out in solution, in a slurry, or in the gas phase. The monomer or comonomers used are preferably although not necessarily addition polymerizable monomers containing one or more degrees of unsaturation. Such monomers include olefinic and vinyl monomers such as ethylene, propylene, butadiene, styrene, and the like. The polymeric product resulting from the aforementioned reaction may be recovered by filtration or other suitable techniques. If desired, additives and adjuvants may be incorporated into the polymer composition prior to, during, or following polymerization; such compounds include, for example, additional catalysts (which may or may not be polymerization catalysts), pigments, antioxidants, lubricants and plasticizers.

Use as a hydrogen source in batteries and fuel cells: Additionally, the alane polymorphs prepared herein can be used as a hydrogen source in batteries and fuel cells. Alane provides a higher density of hydrogen than liquid hydrogen. Upon thermal or photochemical initiation, alane is theorized to initially produce an alane cation radical and a free electron. Both the cation radical and the electron can separately react with another alane molecule to initiate decomposition that results in the formation of hydrogen gas and aluminum metal. Thus, light, heat, or mobile electrons can be used as initiators to catalyze the decomposition. Accordingly, a composition containing the stabilized α -alane and/or the α' -alane of the invention can be used for controlled release of hydrogen gas in a battery or fuel cell. In general, the alane products of the invention will find utility in hydrogen storage electrodes, particularly negative electrodes, in alkaline storage batteries that comprise a positive electrode, a negative electrode, and an aqueous alkaline electrolyte. In fuel cells, electrochemical devices for continuous delivery of electricity wherein the devices contain a fuel, e.g., a hydrogen source, and an oxidant, the alane products of the invention will find utility as the hydrogen source.

It is to be understood that while the invention has been described in conjunction with the preferred specific embodiments thereof, that the foregoing description as well as the examples which follow are intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

EXPERIMENTAL:

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to carry out the methods of the invention and prepare and use the claimed compounds and compositions. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C and pressure is at or near atmospheric.

15

EXAMPLE 1

SYNTHESIS OF α -ALANE

A reaction flask containing 600 mL of ether and 35 mL of a 1 M ether solution of AlCl_3 was purged with argon. To the solution was then added 6.7 g of solid LiAlH_4 over a period of 15 min. The reaction was stirred for 15 min. and then 45 mL of a 1 M LiBH_4 in ether solution was added. The reaction was stirred for a further 30 min. at room temperature, and then filtered to remove lithium chloride.

The filtrate was transferred to a flask containing a diethyl ether solution of about 50 mole % of sodium borohydride. To the solution was then added 2.5 L of toluene and the solution was stirred for a further 20 min., filtered into a reaction flask, and the reaction flask was connected to a distillation column. The diethyl ether was removed under vacuum by heating the reaction flask to about 60 °C until only about 7 % ether was left in the reaction flask. The reaction flask was then heated at 82-85 °C for about 2 h., and then at 90-93 °C for about 30 min. During heating, white crystalline particles formed that grow in size during the heating period. Following the heating cycles, the white crystalline product was collected by

filtration, washed twice with diethyl ether, and dried under reduced pressure to give the α -alane product.

EXAMPLE 2

5

SYNTHESIS OF α' -ALANE

The solvated alane was produced as in Example 1. After filtration of the ether solution to remove lithium chloride, LiAlH_4 was added to the solution, and the ethereal solution was heated to about 80 °C for 2 h. White crystalline particles form that grow in size during the heating period, and were collected by filtration. The crystalline product was
10 washed twice with diethyl ether, and was dried under reduced pressure to give the α' -alane product.

EXAMPLE 3

15

STABILIZATION OF CRYSTALLINE ALUMINUM HYDRIDE

(a) The α -alane product of Example 1 was slowly added to 10% v/v of aqueous HCl while stirring. The resulting suspension was stirred at room temperature for 2 hours. The solid was collected by filtration, rinsed once with water, ethanol, and diethyl ether, and then dried to a constant weight under reduced pressure.

20

(b) The procedure of part (a) was repeated with an alane stabilization agent, aluminon, in the aqueous HCl (10% v/v).

EXAMPLE 4

STABILIZATION OF CRYSTALLINE ALUMINUM HYDRIDE
WITH SURFACE STABILIZERS

The α -alane product of Example 1 was slowly added to methanol containing
5 aluminon (4% w/v). The methanol slurry was stirred at room temperature for 30 min. and then
methanol was slowly evaporated with gentle heating over a period of 5 h. The solid was
rinsed once with water, ethanol, and diethyl ether, and then dried to a constant weight under
reduced pressure.

10

EXAMPLE 5

EVALUATION OF STABILITY

The α -alane product prepared in Example 3(b) was compared with an α -alane
product prepared without an acid wash workup or surface stabilizers, as follows. Both
samples were stored at about 60 °C, and the percentage decomposition over time was
15 evaluated using a standard Taliani test apparatus. The test results are shown in Figure 1. As
may be seen, the alane product prepared using the method of the invention was significantly
more stable than the alane product prepared using the method of the prior art.

The thermal stability of the α -alane product prepared in Example 3(b) was also
studied by DSC and TGA. In the DSC experiments, the sample did not exhibit the onset of an
20 exothermic reaction until about 162 °C that was followed immediately with a large
endothermic reaction. In the TGA experiments, samples of α -alane of Example 3 rapidly lost
weight between 162-215 °C. The observed mass loss was about 9 to 10 % of the total mass,
and corresponds to the theoretical amount of 10% hydrogen in AlH_3 . In a separate experiment,
the alane did not lose mass at 70 °C in a humid environment after 2 days.

25

EXAMPLE 6

MANUFACTURE OF ENERGETIC COMPOSITIONS

The stabilized α -alane of Example 3(b), ammonium perchlorate, ammonium dinitramide and hydroxyl-terminated polybutadiene, are blended to substantial homogeneity and cured with any one of a variety of curing agents including, but not limited to, hexane 1,6-diisocyanate, toluene diisocyanate and isophorone diisocyanate. The proportions of fuel and oxidizer can be varied arbitrarily within the constraint of the loading tolerance of the binder system, so as to optimize any aspect of performance.

CLAIMS:

1. A method for preparing α -AlH₃, comprising the steps of:
 - (a) reacting an alkali metal hydride with AlCl₃ in a solution of diethyl ether to form
5 an initial AlH₃ product in a reaction mixture, along with an alkali metal chloride;
 - (b) removing the alkali metal chloride from the reaction mixture by filtration;
 - (c) adding an excess of toluene to the filtrate resulting from step (b), providing a diethyl ether-toluene solution;
 - (d) heating and distilling the diethyl ether-toluene solution to reduce the amount of
10 diethyl ether in the solution, until a precipitate is formed;
 - (e) isolating the precipitate; and
 - (f) adding the precipitate to an acidic solution effective to dissolve and thus remove materials other than α -AlH₃.
- 15 2. The method of claim 1, further comprising:
 - (g) isolating α -AlH₃ from the acidic solution.
- 20 3. The method of claim 1, wherein the acidic solution of step (f) contains an α -AlH₃ stabilizing agent.
- 25 4. The method of claim 3, wherein the α -AlH₃ stabilizing agent comprise a compound that coordinates to the Al³⁺ ion.
5. The method of claim 4, wherein the α -AlH₃ stabilizing agent is aluminon.
6. The method of claim 4, wherein the α -AlH₃ stabilizing agent is 8-hydroxyquinoline.
7. The method of claim 4, wherein the α -AlH₃ stabilizing agent is catechol.

8. The method of claim 3, wherein the α -AlH₃ stabilizing agent is an electron donor or an electron acceptor.

5 9. The method of claim 8, wherein the electron donor or electron acceptor is selected from the group consisting of tetrachlorobenzoquinone, diphenylamine, tetracyanoethylene, 7,7,8,8-tetracyanoquinodimethane, tetrathiafulvalene and tetrakis(dimethylamino)ethylene.

10 10. The method of claim 1, further including, after step (b) and prior to step (d), adding an additional alkali metal hydride to the reaction mixture and/or the diethyl ether-toluene solution, followed by a further filtration step, wherein the additional alkali metal hydride may or may not be the same as the alkali metal hydride of step (a).

15 11. The method of claim 1, wherein the alkali metal hydride is LiAlH₄.

12. The method of claim 1, wherein the alkali metal hydride is LiBH₄.

20 13. The method of claim 1, wherein the molar ratio of the alkali metal hydride to AlCl₃ in step (a) is in the range of approximately 3:1 to 4.5:1.

14. The method of claim 1, wherein the acidic solution is an HCl solution.

25 15. The method of claim 14, wherein the acidic solution is approximately 5% to 15% (w/w) HCl.

16. A stabilized α -AlH₃ product prepared by the process comprising:

- 30 (a) reacting an alkali metal hydride with AlCl₃ in a solution of diethyl ether to form an initial AlH₃ product in a reaction mixture, along with an alkali metal chloride;
- (b) removing the alkali metal chloride from the reaction mixture by filtration;
- (c) adding an excess of toluene to the filtrate resulting from step (b), providing a diethyl ether-toluene solution;

(d) heating and distilling the diethyl ether-toluene solution to reduce the amount of diethyl ether in the solution, until a precipitate is formed;

(e) isolating the precipitate;

(f) adding the precipitate to an acidic solution effective to dissolve and thus remove materials other than $\alpha\text{-AlH}_3$; and

(g) isolating $\alpha\text{-AlH}_3$ from the acidic solution.

17. The stabilized $\alpha\text{-AlH}_3$ product of claim 16, wherein the acidic solution of step (f) contains an $\alpha\text{-AlH}_3$ stabilizing agent.

18. The stabilized $\alpha\text{-AlH}_3$ product of claim 17, wherein the $\alpha\text{-AlH}_3$ stabilizing agent comprise a compound that coordinates to the Al^{3+} ion.

19. The stabilized $\alpha\text{-AlH}_3$ product of claim 18, wherein the $\alpha\text{-AlH}_3$ stabilizing agent is aluminon.

20. The stabilized $\alpha\text{-AlH}_3$ product of claim 18, wherein the $\alpha\text{-AlH}_3$ stabilizing agent is 8-hydroxyquinoline.

21. The stabilized $\alpha\text{-AlH}_3$ product of claim 18, wherein the $\alpha\text{-AlH}_3$ stabilizing agent is catechol.

22. The stabilized $\alpha\text{-AlH}_3$ product of claim 17, wherein the $\alpha\text{-AlH}_3$ stabilizing agent is an electron donor or an electron acceptor.

23. The stabilized $\alpha\text{-AlH}_3$ product of claim 22, wherein the electron donor or electron acceptor is selected from the group consisting of tetrachlorobenzoquinone, diphenylamine, tetracyanoethylene, 7,7,8,8-tetracyanoquinodimethane, tetrathiafulvalene and tetrakis(dimethylamino)ethylene.

24. A method for preparing α' - AlH_3 , comprising the steps of:

(a) reacting an alkali metal hydride with AlCl_3 in a solution of diethyl ether to form an initial AlH_3 product in a reaction mixture, along with an alkali metal chloride;

(b) removing the alkali metal chloride from the reaction mixture by filtration;

5 (c) adding an additional alkali metal hydride and an excess of toluene to the filtrate resulting from step (b), providing a diethyl ether solution containing α' - AlH_3 and optionally other AlH_3 polymorphs; and

(d) removing the α' - AlH_3 from the solution.

10 25. The method of claim 24, wherein the alkali metal hydride of step (a) is LiAlH_4 .

26. The method of claim 24, wherein the alkali metal hydride of step (a) is LiBH_4 .

15 27. The method of claim 24, wherein the molar ratio of the alkali metal aluminum hydride to AlCl_3 in step (a) is in the range of approximately 3:1 to 4.5:1.

28. The method of claim 24, wherein the additional alkali metal hydride is NaAlH_4 or NaBH_4 .

20 29. The method of claim 24, wherein the alkali metal borohydride is LiBH_4 .

30. In a propellant composition comprising a fuel, a binder, and an oxidizer, the improvement comprising using as the fuel the stabilized α - AlH_3 product of any one of claims 16, 17, 18, 19, 20, 21, 22 and 23.

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31. In a method for reducing a functional group in a molecule by reaction with a reducing agent comprising a hydride donor, the improvement comprising using as the hydride donor the stabilized α - AlH_3 product of any one of claims 16, 17, 18, 19, 20, 21, 22 and 23.

32. In a method for reducing a functional group in a molecule by reaction with a reducing agent comprising a hydride donor, the improvement comprising using α' -AlH₃ as the hydride donor.

5 33. In a method for conducting a reaction comprising the polymerization of monomers using a polymerization catalyst comprising a hydride donor, the improvement comprising using as the hydride donor the stabilized α -AlH₃ product of any one of claims 16, 17, 18, 19, 20, 21, 22 and 23.

10 34. In a method for conducting a reaction comprising the polymerization of monomers using a polymerization catalyst comprising a hydride donor, the improvement comprising using α' -AlH₃ as the hydride donor.

15 35. In an alkaline storage battery comprising a positive electrode, a negative electrode comprised of a hydrogen storage material, and an aqueous alkaline electrolyte, the improvement comprising using as the hydrogen storage material the stabilized α -AlH₃ product of any one of claims 16, 17, 18, 19, 20, 21, 22 and 23.

20 36. In an alkaline storage battery comprising a positive electrode, a negative electrode comprised of a hydrogen storage material, and an aqueous alkaline electrolyte, the improvement comprising using α' -AlH₃ as the hydrogen storage material.

25 37. In a fuel cell for continuously delivering electricity, comprising a contained hydrogen source as a fuel, and an oxidant, the improvement which comprises using as said hydrogen source the stabilized α -AlH₃ product of any one of claims 16, 17, 18, 19, 20, 21, 22 and 23.

30 38. In a fuel cell for continuously delivering electricity, comprising a contained hydrogen source as a fuel, and an oxidant, the improvement which comprises using α' -AlH₃ as said hydrogen source.

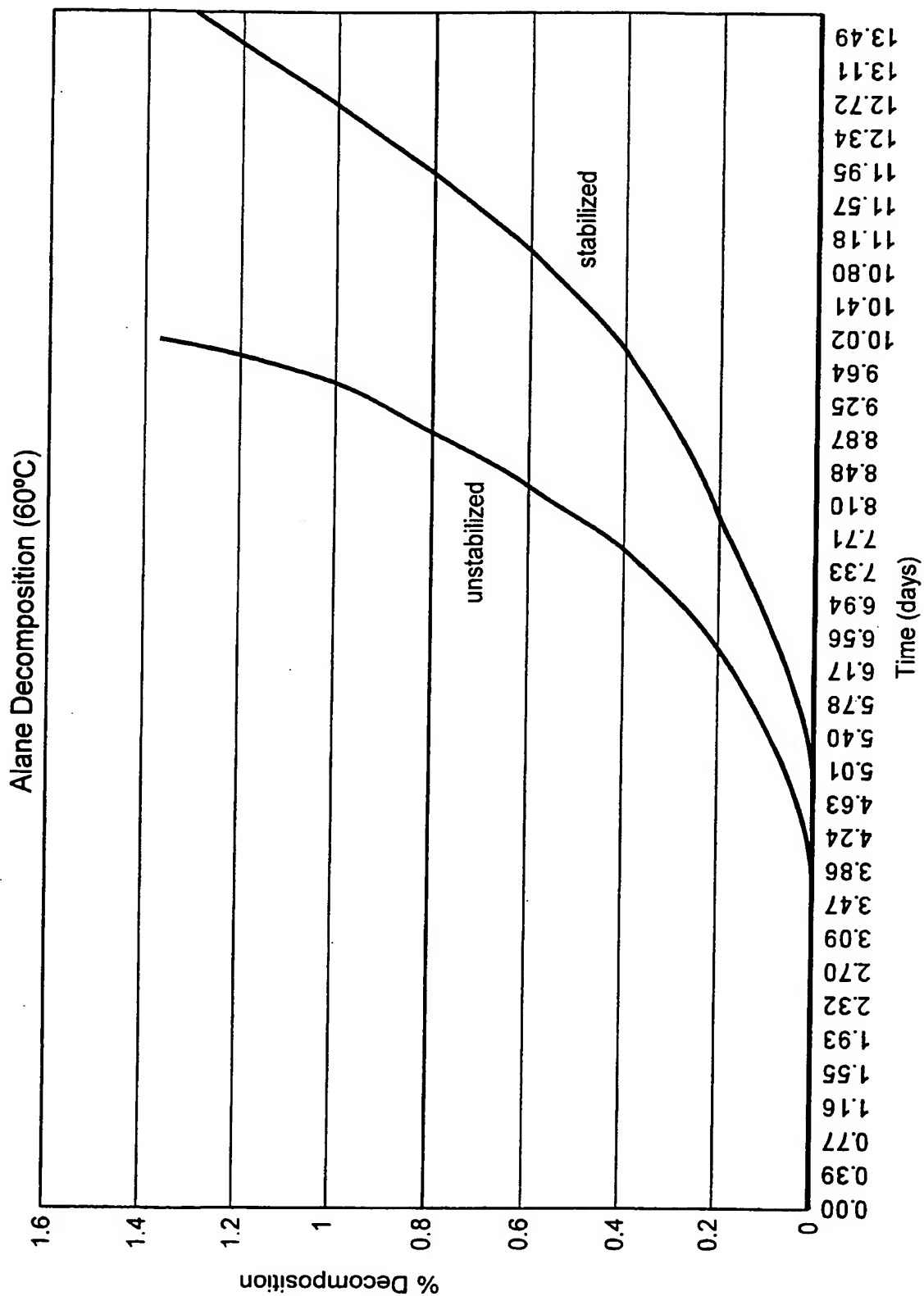


Figure 1

INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/US 00/16137

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B6/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 245 569 A (AEROJET-GENERAL CORPORATION) 25 April 1975 (1975-04-25) claim 1	1
A	US 3 801 657 A (SCRUGGS J) 2 April 1974 (1974-04-02) cited in the application claim 1	1
A	US 3 883 644 A (MATZEK NORMAN E ET AL) 13 May 1975 (1975-05-13) example 1	24
A	US 3 844 854 A (SELF J ET AL) 29 October 1974 (1974-10-29) claim 1	1-3

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Clement, J-P

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/16137

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2245569 A	25-04-1975	NONE	
US 3801657 A	02-04-1974	NONE	
US 3883644 A	13-05-1975	NONE	
US 3844854 A	29-10-1974	NONE	